STUDY OF VOLATILE ORGANIC COMPOUNDS (VOCs), TRACE GASES (OZONE AND NO_X) AND BLACK CARBON AT DAYALBAGH: A SEMI-URBAN SITE

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INTRODUCTION

Hydrocarbons play a significant role in atmospheric chemistry. They can be present in the atmosphere in two physical conditions, depending on their volatility or vapor pressure. If they are volatile, they are present as free molecules in the atmosphere. These types of hydrocarbons are classified as Volatile Organic Compounds (VOCs). On the other hand, if a compound's vapour pressure is low enough it partitions between the gas phase and aerosols, they are denoted as semi-volatile organic compounds (SVOCs). There is no global consensus on defining the exact boundary of the group of volatile organic compounds. In European and Australian legislation, VOCs are organic compounds with a vapor pressure at 25°C of, at least, 10 and 270 Pa respectively, whereas in the USA volatile organic compounds are defined as organic compounds which have negligible photochemical reactivity. Within the group of hydrocarbon, methane takes somewhat special position due its relatively low reactivity and consequently high ambient mixing ratios. Therefore, hydrocarbons with exclusion of methane are sometimes considered as one group: the non-methane hydrocarbon (NMHCs).

Non-methane hydrocarbons (NMHCs), a class of volatile organic compounds (VOCs), are an important component of urban air pollution because of their role in the formation of tropospheric ozone (O_3) and, in the case of aromatic NMHCs, the formation of secondary organic aerosols *(Derwent, 1995; Odum et al., 1997)*. In NO_x rich urban environment dominating anthropogenic sources of NMHCs include automotive exhaust, gasoline evaporation, and emissions from commercial and industrial use of solvents *(Nelson et al., 1983)*. In urban area where NMHC concentrations are high, OH radical attack on the various NMHCs play a critical role in atmospheric photochemical reaction cycle *(Blake et al.1992)*.

Volatile organic compounds (VOCs) are of high interest for atmospheric chemistry and biogeochemistry as they contribute to the oxidative capacity of the atmosphere, to particle production and to the carbon cycle. Carbonyls (low molecular weight ketones and aldehydes) and volatile organic compounds (VOCs) are ubiquitous in the atmosphere. They are of concern for their adverse effects to vegetation and human health, such as toxic, mutagenic and possible carcinogenic effect. They have both anthropogenic and biogenic origins *(Beisenthal et al., 1998)*. In urban areas, they are directly emitted into the air by industrial

processes, vehicular emissions and other stationary substance as primary sources; carbonyls are also produced by photochemical oxidation of VOCs and heterogeneous interactions of aldehydes as secondary pollutants *(Christensen et al., 2000)*. Photo-oxidation of VOCs and direct biogenic emission are important sources in rural areas. Compared with the urban atmospheric environment, there were only a few studies on atmospheric carbonyls in rural regions, to our knowledge, data on the diurnal variations of atmospheric concentrations of carbonyls and VOCs are also limited. A large data is needed regarding the implications and roles of carbonyls and VOCs in the global atmospheric environment *(Mohamed et al., 2002)*.

Volatile organic compounds (VOC) and nitrogen oxides (NO_x) are associated with the formation of photochemical oxidants and elevated surface ozone (O_3) levels in urban areas. Although three-dimensional photochemical models provide effective means of evaluating the sensitivity of VOC or NOx to ozone formation, the accuracy of predictions has been difficult to test empirically, because of model assumptions, including those related to emission inventory and micrometeorology *(Fujita et al., 1992; Sillman, 1995)*. Several alternative approaches have therefore been developed to determine the ozone sensitivity to the reduction of VOC and NO_x emissions. One such approach is to use photochemical indicator species, such as hydrogen peroxide (H_2O_2), nitric acid (HNO_3), and reactive nitrogen species, or ratios of such species *(Penga et al., 2006)*.

VOCs comprise a large number of different species belonging to the isoprenoids (isoprene and terpenoids) as well as alkanes, alkenes, carbonyls, alcohols, acids, esters and ethers. For vegetation emissions, the most prominent compounds are ascribed to be isoprene and monoterpenes. Another complicating factor with oxygenated compounds is that both emission and deposition are possible, depending on the environmental conditions *(Staudt et al., 2000)*. More needs to be known about VOCs in the atmosphere, especially in the tropics, to fully understand their sources and fates within the fields of atmospheric chemistry and biogeochemistry *(Kesselmeier et al., 2002)*.

In the mid-1980s, it became clear that research on volatile organic compounds (VOCs) should have been extended to biogenic components because they are capable of forming ozone with the same or higher efficiency than the anthropogenic hydrocarbons. It is known that isoprene is one of the most abundant biogenic VOCs mainly produced by plants via photosynthetic activities and can contribute up to ~ 50% of the atmospheric burden of non-methane hydrocarbons (NMHCs) in rural areas *(Guenther et al., 1993)*. Isoprene emission rates by plants are affected by several factors such as temperature, light intensity, plant and leaf age, water deficit, and air pollution. Temperature and light intensity are the most important factors

controlling biogenic emissions of isoprene *(Xiaoshan et al., 2000)*. In the lower atmosphere, isoprene is highly reactive and plays an important role in the photochemistry, and acts as a sink of oxidants (such as O_3, OH and NO_x). Photochemical reaction of isoprene in the lower atmosphere, especially in polluted urban areas, can contribute a significant quantity of ozone to the ambient air in densely populated areas. Although sources and abundance of isoprene have been studied extensively, it is becoming clear that, through systematic observation in different environments and time periods, isoprene flux is highly variable, and thus its impact on ozone formation is also variable *(Bing et al., 2006)*.

The NO_2 formation in urban atmospheres is mainly due to the NO oxidation by peroxy radicals produced by photooxidation of nonmethane hydrocarbons (NMHC). The main chemical sink of NO_2 is highly water-soluble a photochemically relatively long-lived nitric acid (HNO_3):

$$NO_2 + HO\ (+M) \rightarrow HNO_3\ (+M)$$

NO_x can also be removed during darkness by gas phase reactions that produce N_2O_5, which subsequently reacts with H_2O on aerosol surfaces such as sulfate, sea-salt, or soil dust particles to produce HNO_3, which may be removed from the gas phase by incorporation into aerosols:

$$NO + O_3 \rightarrow NO_3 + O_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2\ (+M) \rightarrow N_2O_5\ (+M)$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

In polluted air, oxidation reactions that involve the more reactive hydrocarbons can sequester part of the NO_x through the production of peroxy-acetyl-nitrate (PAN), a thermolabile gas. The potential importance of PAN as a reservoir species of NO_x under low-temperature conditions has since been confirmed by many atmospheric measurements *(Crutzen et al., 1979; Bradshaw et al., 2000)*.

Carbon monoxide (CO) serves to produce ozone and affects global ozone concentrations by its effect on OH and HO_2 concentrations. Observations indicate that CO concentrations in remote regions of the Southern Hemisphere have roughly half the levels observed in the Northern Hemisphere *(Hamilton et al., 1991)***.** In the troposphere, hydroxyl free radicals (OH) oxidize carbon monoxide (CO) to form hydroperoxy radicals (HO_2) which involves in the tropospheric ozone formation *(Levy, 1971)*. Within the atmosphere, the major CO source is oxidation of methane by OH, producing formaldehyde (HCHO) and then carbon monoxide. The tropospheric abundances of CO and CH_4 thus become important indices of the tropospheric

oxidizing capacity, represented most specially by the concentrations of ozone and hydroxyl free radicals *(Wang et al., 1999)***.**

Ozone is a secondary pollutant that is formed in the troposphere from a complex series of sunlight driven reactions between nitrogen oxides, carbon monoxide, and hydrocarbons particularly NHMC's (non-methyl hydrocarbons), and it is also transported into the troposphere from the stratosphere. Although substantially more ozone is produced and destroyed in the troposphere than the amount supplied from the stratosphere, the supply of stratospheric ozone remains very important and is, in fact, a prerequisite for initiation of the photochemical reactions in the troposphere that can lead to ozone production or loss *(Crutzen et al., 1999)*. Ground-level ozone is formed from complex photochemical reactions of precursor volatile organic compounds (VOCs) and nitrogen oxides (NO_x). VOCs and NO_x come primarily from anthropogenic activity emissions, of which transportation emissions are the major contributor.

Ozone concentration is highly variable whose concentration depends on several meteorological parameters viz., temperature, relative humidity, solar radiation, wind speed and wind direction, hence, understanding the behavior of O_3 in the urban atmosphere is very complex. Ozone levels are typically expressed in parts per billion by volume (ppbv), which represents the fraction of molecules represented by ozone. In continental areas far removed from direct anthropogenic effects, ozone concentrations are generally 20 - 40 ppb. In rural areas downwind of urban centers, ozone concentrations are higher, typically 50 - 80 ppb, but occasionally 100 - 200 ppb. In urban and suburban areas, ozone concentrations can be high (well over 100 ppb), but peak for at most a few hours before deposition and reaction with NO emissions cause ozone concentrations to decline *(Lin et al., 2007)*.

A scientific review by the US Environmental Protection Agency (EPA) of the effects of O_3 found that exposure to ambient O_3 levels is linked to such respiratory ailments as asthma, inflammation and premature aging of the lung, and to such chronic respiratory illnesses as emphysema and chronic bronchitis. Detrimental effects on vegetation include reduction in agricultural and commercial forest yields, most crops in the world are grown in the summer when O_3 photochemical production and resulting concentrations are at their most elevated and are frequently sufficient to reduce crop yields. Besides the above harmful effects Ozone is a greenhouse gas too and it is also a precursor for the highly reactive OH radicals, which determine the chemical composition of the troposphere *(Logan et al., 1981)*. Hence understanding of tropospheric ozone is very important.

Mono-carboxylic acids (MCAs) and di-carboxylic acids (DCAs) are important groups of organic compounds identified in the atmospheric aerosols *(Limbeck et al., 2001)*. Formic and acetic acids, the dominant species of the organic acids in the tropospheric aqueous and gaseous phases, are also ubiquitous in aerosol particles; oxalic acid has been detected as the major fraction of water-soluble organic compounds in urban, rural and even remote background air *(Wang et al., 2002)*. Since carboxylic acids are highly water-soluble, they have the potential to modify the hygroscopic properties of atmospheric particles, including their ambient size and cloud condensation nuclei activity. Weak organic acids could contribute ~ 40% and ~ 60% to the free acidity in precipitation at urban and remote areas respectively *(Likens et al., 1987)*.

Oxalic acid was the most abundant carboxylic acids in aerosols. Formic and acetic acids displayed different seasonal variations, and the variations of these acids were consistent among different sites in urban area. Formic and acetic acids had mass both in the fine and in the coarse modes, while oxalic acid predominated in the fine mode. Acetic-to-formic acid ratio (A/F) was used to distinguish the primary sources and the secondary sources, and it indicated that the contribution of the primary sources was higher at rural site than at urban sites. Carboxylic acids have several different sources, including the primary emissions from fossil fuel combustion and biomass burning, homogeneous photochemical oxidation of organic precursors from both anthropogenic and biogenic origin *(Wang et al., 2007)*. Reaction of ozone with olefins leads to the formation of carbonyls and their oxidation products; Acetic and formic acid.

Carbon is a significant component of urban aerosols. Elemental carbon (EC, i.e. black or graphitic carbon, or soot) is a primary pollutant released during incomplete anthropogenic or natural combustion. Primary organic carbon (OC) particulate matter (PM) is similarly emitted during combustion, but is also associated with biogenic releases**.** An additional secondary organic component results from the condensation of semi volatile organic vapours to particle surfaces, and via atmospheric oxidation reactions. EC and OC are not traditionally part of long-term air pollution monitoring networks due to the complexity and cost of analysis, despite the potential importance of these PM components in determining health impacts. This is despite the dominance of carbon in urban airborne particulate matter, especially in the fine fraction to which urban populations are exposed. EC is a good indicator of primary combustion emissions, particularly for vehicular emissions in urban areas, since it is unaffected directly by volatilisation losses due to temperature fluctuations *(Kendall et al., 2002)*. Recent field, laboratory and 0simulation studies indicate that carbonaceous aerosols may interact heterogeneously with ozone and precursors to influence ozone

variability. Due to their aggregate structure, atmospheric BC particles offer a large surface area for heterogeneous interactions with reactive gases such as ozone, NO_2, OH and HO_2 *(Bhugwant et al., 2001)***.**

The present study aims at explain the relationship between ozone forming species (VOCs & NO_x) and ozone loss reactions. Ozone is destroyed by reaction with olefins leading to formation of carbonyls including formic and acetic acids. In addition ozone levels also decreases in presence of Black Carbon. There are no such studies from India reporting simultaneous production and loss process of ozone. The present study aims at filling this void.

LITERATURE REVIEW

Non-methane hydrocarbons (NMHCs), a class of volatile organic compounds (VOCs), are an important component of urban air pollution because of their role in the formation of tropospheric ozone (O_3) and, in the case of aromatic NMHCs, the formation of secondary organic aerosols *(Derwent et al., 1995)*. Many species, such as benzene and n-hexane, are known to affect human health. NMHCs are emitted by both anthropogenic and biogenic sources, although in most urban environments the anthropogenic sources are dominant. Anthropogenic emissions are from both mobile sources, namely automobiles, and stationary sources, such as power plants and industrial complexes. In the urban troposphere, transportation-related emissions normally constitute a large fraction of NMHC sources *(Colvile et al., 2001)*. Some aromatic species, such as toluene, are used in industrial processes, which can make their transportation fraction relatively less significant. The lighter alkanes (C2–C4) are not strongly associated with vehicular emissions, but are found as components of other fuels such as natural gas and liquefied petroleum gas (LPG) *(Blake et al., 1995)*.

In polluted environments the photo-oxidation of NMHCs in the presence of nitrogen oxides (NOx = $NO+NO_2$) leads to the formation of the secondary pollutant ozone (*Seinfeld, 1989*). The initial step in the production of ozone is the reaction between a NMHC and the hydroxyl radical (OH). Therefore, the relative contributions of individual NMHC species to ozone formation vary based on each compound's rate of reaction with OH. These rates are well studied for the most abundant NMHCs *(Atkinson,2000)* and predictions of ozone production can be made when mixing ratios of ozone precursors are known .The ambient NMHC mixing ratios, ratios of NMHCs to CO are examined, which are useful for understanding the magnitude of hydrocarbon pollution, these can vary widely within a city and between different cities as a result of a number of factors such as dilution and differences in source strengths, as well as local meteorology and geography. Normalizing to an urban tracer accounts for these factors and provides insight into relative mixing ratios, allowing for a more useful comparison of measurements from different locations and cities.

Carbon monoxide, a product of incomplete combustion, is commonly used as a marker for vehicular emissions and is strongly associated with urban pollution. Therefore, examination of NMHC to CO ratios allow for the comparison of otherwise highly variable NMHC mixing ratios. Relatively few speciated hydrocarbon studies have been conducted in multiple US cities. The most comprehensive study was carried out by the United States Environmental Protection Agency (EPA) from 1984 to 1986 in 39 different US

cities *(Evans et al., 1992)*. Samples in that study were collected during the morning hours (between 6 am and 9 am) and at one or two sites in each city. Speciation of NMHC was determined for 15% of those samples, selected because they were collected during periods of high ozone or had unusually high total NMHC *(Bakera et al., 2008)*.

Reactivity quantifies a VOC's potential to produce ozone. Different VOCs can produce vastly different amounts of ozone. Ethene (C_2H_4), for example, can produce over 14 times more ozone than ethane (C_2H_6) under the same conditions. The maximum incremental reactivity (MIR) to calculate VOC limits for aerosol coatings, such that the reduction of ozone formation would be equivalent to a much larger and more technically infeasible VOC mass reduction. This action was approved as a pilot project by the United States (U.S.) Environmental Protection Agency (EPA) in 2005. The EPA issued guidance encouraging use of VOC reactivity information in the development of ozone control measures, and recently finalized national regulations using the MIR to regulate VOC content in aerosol coatings. Although research indicates that a reactivity-based VOC control policy has potential for larger decreases in ozone than indiscriminate VOC mass-based reductions *(McBride et al., 1997)***.**

Radiative, transport and chemical processes concur to determine the ozone (O_3) concentration in the troposphere. Photochemical production from nitrogen oxides (NO_x) coupled with decomposition of volatile organic compounds (VOCs), methane (CH_4) and carbon monoxide (CO) by the hydroxyl radical (OH), mainly determines O_3 level in the free troposphere. In the boundary layer, elevated O_3 concentrations usually occur during pollution events. In fact, during specific fair weather conditions (i.e., atmospheric stability, high pressure), solar radiation works efficiently on O_3 precursors *(Cristofanellia et al., 2007)*.

The residence time (life cycle) of tropospheric O_3 varies according to season and altitudes between a few days (5–8) and a few weeks (3–15). Tropospheric O_3 is not only a chemically active component, but also an important greenhouse gas. Tropospheric O_3 changes contribute roughly $0.35 W/m^2$ (about 8–15%) to the total radiative forcing associated with the greenhouse gas increase since pre-industrial times *(Brasseur et al., 1998)*.

The dependence of ozone production on initial amounts of VOC and NO_x is frequently represented by means of an ozone isopleths diagram. These isopleths are three-dimensional plots of daily maximum hourly average ozone concentrations that are generated in mixtures with various initial non-methane organic compounds and NO_x concentrations. The isopleths are calculated using the EKMA (Empirical

Kinetic Modelling Approach) technique. Due to the chemical coupling of ozone and nitrogen oxides, the levels of O_3 and NO_2 are inextricably linked. Therefore, the response to reductions in the nitrogen oxides emissions is remarkably not linear and any resultant reduction in the level of nitrogen dioxide is invariably accompanied by an increase in the air concentration of ozone *(Nicolas et al., 2005)*.

The abundance of tropospheric O_3 is increasing at many sites over the globe *(Logan et al., 1999)* and expected to rise significantly throughout the 21st century (IPCC, 2001). Asia, in particular is experiencing serious air pollution, including ozone, as a result of population growth and increased fossil fuel consumption due to demand for economic growth. Economic risk assessment of the pollutants requires an accurate and complete understanding of the gridded concentrations of the primary and secondary species of the pollutants. An accurate reproduction of particular pollution episodes can help in disaggregating the different sources of pollution contributing to emissions in a given region, thereby allowing an identification of the most responsible sources.

Indian region is vast in area with lot of diversity in types and quantum of anthropogenic activities and, therefore, the impact of ozone is difficult to gauge with the few measurements available. In general, there have been no systematic simultaneous measurements of surface ozone and its precursor gases over the Indian region. Shende et al. (1992) reported limited measurements of the surface ozone over the Indian region. Recently, Jain et al. (2005) reported increased surface O_3 at Delhi. Chand and Lal (2004) also measured elevated surface O_3 (70–110 ppbv) during afternoon hours at rural sites in downwind direction of major industrial region of Gujarat (India) *(Mittal et al., 2007)*.

Reddy et al. (2008) studied the diurnal and seasonal variation in surface ozone and its precursor gases at a semi-arid site Anantapur (India) and reported that NO_x and CO levels were the highest during morning and late night hours at this site. They showed that the annual average mixing ratios of oxides of nitrogen (NO_x) and CO were 3.9 $\pm$0.6 ppbv and 436$\pm$64 ppbv, respectively.

Further they reported ozone concentrations increase during the day, reaching maximum around local noon. However, the diurnal minimum is reached about an hour after sunrise but not during night. They studied the diurnal variation and found that ozone concentrations are much higher in winter and summer than in autumn. The average ozone during noon hours in autumn months in about 25 ppbv, it becomes as high as 50 ppbv during winter and summer months.

Kumar et al. (2010) studied variations in surface ozone at Nainital, a high-altitude site in the central Himalayas and found that diurnal variations in ozone do not show the daytime photochemical build-up

typical of urban or rural sites. The seasonal variation shows a distinct ozone maximum in late spring (May; 67.2 ± 14.2 ppbv) with values sometimes exceeding 100 ppbv and a minimum in the summer/monsoon season (August; 24.9 ± 8.4 ppbv). *Reddy et al., (2012)* studied the influence of the boundary layer evolution on surface ozone variations at a tropical rural site (Gadanki) in India and found that Daytime average boundary layer height varied from 1.5 km (on a rainy day) to a maximum of 2.5 km (on a sunny day). They observed that the days of higher ozone mixing ratios are associated with the higher boundary layer height and *vice versa*.

Nishanth et al. (2012) studied surface Ozone (O_3) and Oxides of Nitrogen (NO_x) measurements in the ambient air over Kannur University Campus (11.9º N, 75.4º E, 5m), Kerala State, India. They also studied the diurnal profile and the mixing ratio of surface O_3 and NO_x ($NO+NO_2$). *Swamy et al. (2012)* monitored the surface level ozone (O_3), nitrogen oxides (NO_x = NO_2 + NO), volatile organic compounds (VOCs), black carbon (BC) and meteorological parameters at an urban site in Hyderabad using different trace gas monitors. The diurnal variation and weekend/weekday of O_3 and its precursors was studied in winter, summer and monsoon. The annual mean of NO_x and BC concentrations at weekend were observed to be lower than weekday by about 10% and 9%, respectively.

Formic (HCOOH, hereafter FA) and acetic (CH_3COOH, hereafter AA) acids are among the most abundant and ubiquitous trace gases in the atmosphere. They have been detected in remote, rural, polar, marine and urban environments in the gas-phase as well as in clouds and in aerosols *(Keene et al., 1988)*. Sources of FA and AA include direct emissions from biomass burning, bio fuel, fossil fuel, soil, vegetation, as well as secondary production from gas-phase and aqueous photochemistry *(Chebbi et al., 1996; Khare et al., 1999)*.

The most field measurements show a remarkable correlation between FA and AA suggesting similar sources. The sources of FA and AA remain, however, very poorly understood and several investigations have pointed to large inconsistencies between measurements and model predictions. Sinks of FA and AA are better understood. Both acids are relatively long-lived in the gas-phase with respect to OH photo oxidation (FA - 25 days and AA - 10 days at T =260K). Because both gases are very soluble, their primary atmospheric sink is thought to be deposition. Irreversible uptake on dust can also be important regional sink .Better constraints on the budget of FA and AA are important to understand patterns of rain acidity particularly in remote regions. More generally, since FA and AA are major trace gases in the atmosphere

and have few anthropogenic sources, the study of their budget offers a glimpse at the interaction between the biosphere and the atmosphere *(Paulot et al., 2011)***.**

The major sinks of carboxylic acids are dry and wet deposition as a result of their low reactivity towards OH andNO_3. However, the chemical loss via reaction with OH is poorly constrained resulting from the uncertainty in the reported rate coefficient. The modelled atmospheric lifetime of formic acid has been calculated to be 2-3 days. Global models under predict formic acid concentrations especially in the marine boundary layer where [HC(O)OH] can be underestimated by a factor of 10–50, this discrepancy has been attributed to missing sources such as higher biogenic emissions during the growing season *(Rinsland et al., 2004)* and ageing of organic aerosols . Also, the oxidation of VOC precursors leading to the production of formic acid has been suggested to be a significant source *(Arlander et al., 1990)*, for instance the ozonolysis of ethene. Ethene emissions have been estimated to be about 15 Tg yr^{-1} with about 162 Gmol $yr^{-1}$from the oceans, and the presence of a major formic acid-producing reaction channel would therefore be of major importance to atmospheric chemical modelling *(Leather et al, 2012)*.

Black Carbon is emitted into the atmosphere as a byproduct of all combustion processes (vegetation burning, industrial eluents and motor vehicle exhausts). It is one of the important constituents of ambient particulate matter *(Novakov, 1984)*. BC is inert in the atmosphere as a result of its chemical structure and due to its predominant submicron size; its main atmospheric sink is wet deposition *(Ogren et al., 1984)*. When rain is sparse, these particles may accumulate in the tropospheric reservoir and disturb atmospheric radiation and chemical balances. For example, it has also been shown that BC can interact with other gaseous species present in the atmosphere *(Lary et al., 1997)*. BC is one of the main products among the array of pollutants that are emitted by mobile sources. Consequently, BC aerosol may cause environmental as well as harmful health elects in densely inhabited regions *(Wu et al., 1998)*.

Global climate forcing by black carbon (BC) aerosols is uncertain in magnitude. The Intergovernmental Panel on Climate Change estimated a global mean BC forcing of 0.1 W/m^2 in their 1996 report, but in 2001 they raised this to 0.3 $W/m^{2.}$ Others suggest that the BC forcing is probably larger, 0.5 W/m^2 or more. The BC forcing needs to be known accurately for the sake of interpreting past climate change, projecting future change, and developing the most effective strategies for mitigating anthropogenic climate change *(Sato et al., 2003)*.

Black carbon is essentially a primary pollutant; OC consists of a complicated mixture of species from both primary sources and secondary sources. SOCs are produced in the atmosphere via various chemical and physical transformation processes involving the oxidation of volatile organic reactive gases (VORGs) with reactive species such as ozone, hydroxyl and NOx radicals followed by coagulation/condensation onto the pre-existing aerosol particles becoming a part of aerosols already present in the atmosphere *(Ram et al., 2008).* BC showed a negative correlation with ozone concentration and is attributed to the fact that a higher concentration of BC provides more surface area for catalytic reaction for destruction of tropospheric ozone *(Badri et al., 2007).*

Different studies have been conducted in India on ozone and its precursors (NOx and VOCs). Several studies deal with respect to VOCs; Their distribution and sources, some studies report BC measurements from different parts of India. However studies on carbonyls and organic acids are comparatively limited. Despite all these studies there are absolutely no reports which simultaneously present ozone forming process and ozone breakdown reactions. The present study is an attempt to bridge this gap.

OBJECTIVES

On the basis of above literature review it is evident that there have been no systematic and simultaneous measurements of surface ozone and its precursor (NO_x and VOCs) and its loss process.

With this in view the present study has been designed with the following objectives:

- To determine the levels of VOCs and study their seasonal trends.
- To study the diurnal and seasonal trends of ozone and its precursor (NO_x).
- To explore the ozone loss processes through

  (A) Organic Acids

  (B) Black Carbon

METHODOLOGY

SITE DESCRIPTION

The sampling will be carried out on the roof of Science Faculty, Dayalbagh Educational Institute. Dayalbagh (semi-urban site), Agra. Agra is located in the north central (27°10' N, 78°05' E) part of India which is about 200 km southeast of Delhi. It is a semiarid area characterized by loose, sandy, and calcareous soil prone to erosion. Vegetation is scarce and dominated by xerophytic plants. Climatically, Agra is hot and dry during the summer and cool in the winter. The annual rain fall is about 650 mm with 90% being received during monsoon season (July–September). Winter is associated with greater calm periods while during the summer and monsoon strong surface winds are observed. Maximum and minimum temperatures in summer are normally 45°C and 25°C, respectively, while in the winter it ranges between 10°C to 3°C. Relative humidity is highly variable from 25–99%. During winters, the winds blow from the NE, E and SE sectors with a calm period of approximately 75%.

Apart from the local sources Mathura refinery and Firozabad glass industries are both situated at a distance of 40 km from Agra. National Highway lies about 2 km from the sampling site. Although there are no industries in the immediate vicinity of the sampling site, during the monsoon, site becomes downwind with respect to the city's pollution sources. The prominent wind directions during the monsoon are SW, S, SE and E, which correspond to the industrial sectors of the city.

Ozone and NO_X

Ozone and NO_x in ambient air will be measured simultaneously for every 5 min interval with Thermo Scientific instruments. These measured values are averaged to attain daily and monthly concentrations.

Auto-sampling is made at 10 meters elevation above the ground level. Continuous measurement of O_3 concentration will be done by using Model 49i; Thermo Scientific, USA. The operating principle is that, O_3 molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light absorbed is directly related to the O_3 concentration as described by the Beer-Lambert law. Lower detection limit of the analyzer is 1 ppbv with the response time 20 seconds. The O_3 analyzer is calibrated by the in situ generation of O_3 using O_3 generator.

NO_x measurement will be done by using Model 42i; Thermo Scientific, USA. The analyzer works on the principle that NO and O_3 react to produce a characteristic luminescence with an intensity linearly

proportional to the NO concentration. To quantify the NO_2 concentration it must be transformed into NO before involving in chemiluminescent reaction. NO_2 is converted to NO by molybdenum heated to about 325°C. Lower detectable limit of NO_x analyzer is 0.40 ppbv; with response time 40 seconds.

VOCs

Sampling will be carried out by active grab sampling method using a battery- operated pump. A battery operated portable sampling pump (SKC 224-XR) will be used to draw air at the rate of 2l min^{-1} through SKC adsorption cartridge containing activated charcoal (60–80 mesh). The sampling pump will calibrate by an electronic digital flow calibrator. The sample tubes will be placed in polythene bags that seal tightly and kept in a box in a freezer until analysis. Analysis will be done by Shimadzu gas chromatograph (GC-17 A) equipped with a flame ionization detector (FID), BP1 capillary column (25m length and 0.3mm internal diameter), and GC Solution software. GC oven will programmed for 50ºC hold for 4min and ramped to 250ºC at a rate of 10ºC /min with 10min hold at 250ºC.

Organic Acids

HCOOH and CH_3COOH will be collected from the atmosphere using the aqueous nebulizer or mist chamber. In this method, the air to be sampled in a round glass chamber which contains the extracting solution (in this case water). As the air passes through the second nebulising nozzle, water from the chamber is aspirated into the air stream and fine mist generated. These droplets provide a large surface area for the absorption of water-soluble gases from the sampled air. Samples will be analyzed by injected into the ion chromatograph (Dionex ICS-1100).

Black Carbon

The aerosol samples for the $PM_{2.5}$ will be collected using HVS Envirotech APM550 Respirable Dust Sampler operated at a flow rate of 16.6 L/min for 24 hrs on 47 mm Quartz fiber filter paper. Before exposure, the quartz fiber heated in a muffle furnace at 800 $^{\circ}C$ for 6 h to remove organic impurities. Before and after sampling the filter will kept in the desiccators for 24 h, and then weighed on an electronic microbalance (Mettler) to determine the PM mass. After weighing the samples wrapped in aluminium foil will be sealed in polyethylene zip lock bags and stored in deep freezer at -4 $^{\circ}C$ until the time of chemical analysis to prevent the evaporation of volatile components.

1.5 cm^2 punch was cut from the loaded 47 mm quartz fiber filter paper and analyzed for OC EC concentration using EC-OC analyzer (Sunset Laboratory, USA, model 2000). The analytical procedure for OC-EC consisted for two stages. In the first stage, OC is volatilized from the sample in a non oxidizing atmosphere (100% He) through a step-wise heating (340, 500 and 615 $^{\circ}C$ maintained for 60s and at 870 $^{\circ}C$ for 90s). in the second stage, the oven is cooled to below 550 $^{\circ}C$ for 60s, a mixture of oxygen and helium gas (2% +98, by volume) is then introduced and oven temperature is increased step-wise to 900 $^{\circ}C$ (550, 625, 700, 775 and 850 $^{\circ}C$ maintained for 45s and 900 $^{\circ}C$ for 120s). The thermograph produced provides four OC fraction (OC_1, OC_2, OC_3, OC_4) during first stage of heating and those produced in the second step of heating liberates pyrolyzed carbon (PC) and three EC fraction (EC_1, EC_2, EC_3).

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